ARKIV FÖR FYSIK Band 15 nr 41

Communicated 28 January 1959 by Erik Rudberg and Kai Siegbahn

Effect of spectrometer window on the K absorption edge of Au

By Olof Beckman, Bertil Axelsson and Pär Bergvall

With 6 figures in the text

1. Introduction

The need of accurate determinations of the atomic binding energies has lately become acute in view of the demands of high-precision beta spectroscopy. For heavier elements, the most accurate value for the K level is obtained from the L_{III} and L_{II} values by addition of the energies of the $K\alpha_1$ and α_2 emission lines, which can be measured with high precision. A method for precision measurements of the L levels has been developed at this institute [13].

A direct method of establishing the K level energy is to measure, by crystal diffraction methods, the variation in intensity of the "white" X-radiation transmitted through an absorber. At the critical energy, the characteristic absorption edge appears. The intensity variation is transformed into the variation of absorption coefficient, where the point of inflexion represents the binding energy.

Apart from the difficulty in establishing the point of inflexion, this method involves a systematic error known as the "thickness effect". Parratt *et. al.* [7] have pointed out that every spectrum is distorted by the finite width of the spectrometer window. In the case of an absorption edge the consequence is a shift of the edge towards higher energies. The shift is greater, the greater the contrast of the edge, which means that to a certain extent it should be linearly dependent of the absorber thickness. The correct procedure for the determination of an absorption limit by this method must therefore be to measure the edge with different absorber thicknesses and extrapolate to zero thickness.

Both the above methods of measuring the K binding energy are attempted in the present investigation for the case of gold. For the L_{III} and L_{II} levels, values according to Sokolowski [14] have been used. Measurements of the $K\alpha_1$ and α_2 lines and the K absorption edge for different absorber thicknesses have been made using the 2-meter curved crystal precision spectrometer at this institute. An attempt to account for the observed shift is made with certain assumptions on the shape of the true absorption edge and the spectrometer window.

2. Experimental procedure

The curved crystal precision spectrometer and the van de Graaff generator acting as X-ray source have been previously described [1, 2]. For the Au $K\alpha$ line measurements the X-ray anticathode consisted of a 0.3 mm thick gold layer on

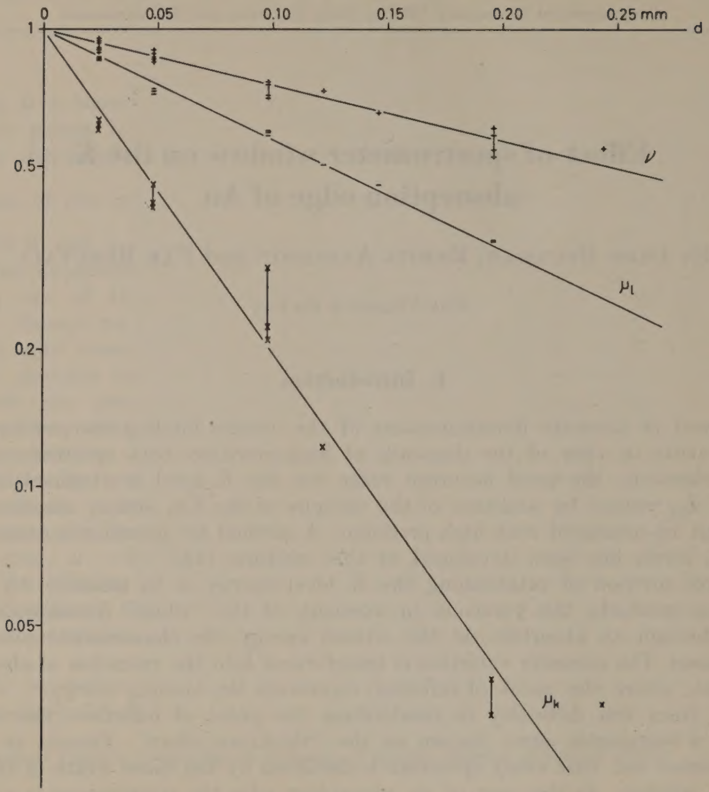

Fig. 1. Semilogarithmic diagram of ratios between transmitted and incident radiation as function of absorber thickness. The curves represent the background (ν) and the coherently scattered radiation on the low-energy (μ_l) and high-energy (μ_k) side of the Au K absorption edge.

a copper plate. For the Au K edge measurements, this was exchanged for a 2 mm thick uranium plate, giving a high yield of bremsstrahlung. The U $K\alpha_1$ line was used as reference for the absorption measurements. This facilitated the determinations as a delineation of the edge was then necessary only in one of the two positions of the spectrometer. The emission line is namely much more quickly and accurately located than the edge.

The absorbers consisted of gold foils of two dimensions. The thicknesses were determined by weighing. They were placed in a slide in front of the detector collimator. Eleven measurements were made, representing 4 different absorber thicknesses ranging from 0.02 mm to 0.2 mm.

In order to determine the absorption limit, the intensity (I) variation recorded with the spectrometer must be transformed into the variation of absorption coefficient (μ):

$$I - I_b' = (I_0 - I_b)\, e^{-\mu d}. \qquad (1)$$

d stands for the absorber thickness, I_0 for the primary intensity, and I'_b and I_b for the background with and without absorber.

The background consists of radiation, incoherently scattered, mainly in the curved crystal, passing through the collimator tube and being accepted by the channel discriminator of the scintillation counter. By blocking the collimator entrance with lead, we found other sources of background to be negligible. An exponential decrease of the background with absorber thickness can then be expected:

$$I'_b = I_b \, e^{-\nu d}. \tag{2}$$

Here ν represents a mean absorption coefficient for the radiation accepted by the scintillation detector. I'_b and I_b were determined according to the following. As the crystal and detector are in appropriate positions of a particular wavelength, all of the coherently scattered radiation of this wavelength and the incoherently scattered background is collected by the detector through the collimator tube. If the crystal is turned from this position while the detector is kept fixed, all of the coherently scattered radiation will eventually escape detection, whereas the background will remain substantially the same. From an intensity curve obtained in this way the actual background is easily interpolated. A background measurement was made before and after every edge recording. Additional determinations were made, including other absorber thicknesses, and in Fig. 1 log I'_b/I_b is plotted against d, verifying the relation (2).

Sufficiently remote (400 eV) from the absorption discontinuity the absorption coefficient reaches its "limiting" values μ_l and μ_k on the low and high energy side respectively. The ratio of the corresponding limiting intensities, $(I - I'_b/I_0 - I_b)$, gives as a function of d in the semilogarithmic diagram, Fig. 1, the values of μ_l and μ_k according to eq. (1). The points represent intensity ratios obtained from the edge measurements and additional measurements for a few more values of absorber thickness. The scattering of the points around the straight lines may be taken as an indication of the reliability in the intensity and background determinations.

A spectrometer recording of the intensity variation at the Au K limit is shown in Fig. 2, together with the corresponding variation in μ according to eq. (1). As expected, in view of the relatively great width of the K level, no Kronig–Kossel structure is resolved. The curve shows, within the experimental errors, an arc tan variation and the point of inflexion may therefore be taken to represent the transition from the K level to the first unoccupied level in the Fermi band. For a definition of the point of inflexion we have chosen the point on the curve with the μ value $\frac{1}{2}$ $(\mu_k + \mu_l)$.

3. Experimental results

3.1. *Absorption coefficients*

From the diagram, Fig. 1, the linear absorption coefficients are found:

	Present	Victoreen [15]
μ_k, high energy side	16.2 mm^{-1}	16.3 mm^{-1}
μ_l, low energy side	5.49 mm^{-1}	

As a comparison the value computed from Victoreen's tables is cited.

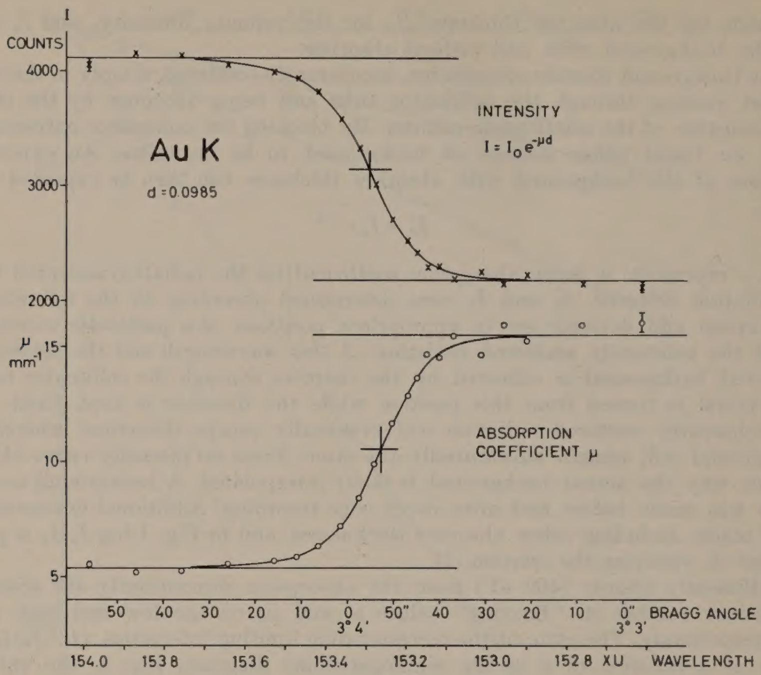

Fig. 2. An experimental curve for Au K, absorber thickness 0.0985 mm. The intensity curve ($\times$) is shown above the corresponding variation in absorption coefficient (○). The asymptotic parts of the curves are determined by experimental points lying outside the diagram.

3.2. *Absorption limits*

In a previous report [2] on the precision curved crystal spectrometer employed here, a calibration of the instrument with use of four well-established X-ray lines is described. These were the $K\alpha_1$ lines of W, Sb, Ag and Mo. Anticipating a forthcoming international agreement on the definition of the X unit by means of the Mo $K\alpha_1$ line as suggested by DuMond, the authors will for the present investigation use the above Mo $K\alpha_1$ measurements as a calibration. They were performed immediately before the Au edge determinations. In view of the large Bragg angle for Mo $K\alpha_1$, the accuracy of the calibration is high, or about 6 ppm.

The value for the instrumental constant and the wavelength value for Mo $K\alpha_1$ used as basis, are the following:

Line	Wavelength, XU	Instrumental constant, XU, 18°C
Mo $K\alpha_1$	707.831	1177.539 ± 0.007

All Bragg angles given below are corrected to 18°C with use of a thermal expansion coefficient for quartz in the $13\bar{4}0$ direction of 14.5×10^{-6} [6].

Table 1. Difference in Bragg angle between U $K\alpha_1$ and Au K, ($\Delta\theta$), for different absorber thicknesses (d). Temperature t°C.

d mm	$\Delta\theta$ Au K − U $K\alpha_1$, 18°C	t°C Au K	t°C U $K\alpha_1$
0.024	40′19.2″	21.8	22.1
0.024	40′20.6″	22.2	22.6
0.024	40′20.5″	24.2	24.4
0.048	40′18.7″	24.2	24.6
0.048	40′20.4″	21.8	22.8
0.048	40′18.9″	21.8	23.1
0.0985	40′18.0″	21.6	22.3
0.0985	40′19.3″	22.8	23.7
0.0985	40′19.2″	22.4	22.7
0.197	40′17.0″	22.5	22.8
0.197	40′16.8″	21.1	21.9

The Bragg angle of U $K\alpha_1$ has been previously determined [2], U $K\alpha_1$: 3°3′33.4″. In Fig. 3 the Bragg angle, wavelength, and energy of the Au K limit are shown as a function of absorber thickness. The straight line has been drawn according to a least squares fit. The size of the shift is found to be:

Shift: 1.77″ ± 0.40″ per 0.1 mm Au
0.020 ± 0.004 XU per 0.1 mm Au

The extrapolated absorption limit for zero thickness is:

Au K: 3°43′53.8″ ± 0.8″
153.275 XU ± 0.010 XU
80.7205 keV ± 0.005 keV ($E \cdot \lambda_s = 12372.44$ XU·keV)

Table 2. Bragg angles, (θ), of Au $K\alpha_1$ and $K\alpha_2$.

Au $K\alpha_1$		Au $K\alpha_2$	
θ 18°C	t°C	θ 18°C	t°C
4°22′44.2″	23.0	4°29′52.0″	22.3
44.6″	22.4	51.8″	22.1
44.2	23.1	52.5	23.3
44.0	23.7	52.5	23.0
44.1	24.6	51.8	23.0
4°22′44.2″ ± 0.3″ 179.816 XU ± 0.005 XU 68.8061 keV ± 0.0018 keV		4°29′52.1″ ± 0.3″ 184.687 XU ± 0.005 XU 66.9914 keV ± 0.0017 keV	

Previous measurements by Ingelstam [5] show good agreement:

Au $K\alpha_1$ 179.822 XU ± 0.010 XU
Au $K\alpha_2$ 184.691 XU ± 0.010 XU

Combining with the L-level energies according to Sokolowski [14], the following is obtained:

L_{II}	13.7337 keV ± 0.0005 keV
$K\alpha_2$	66.9914 keV ± 0.0017 keV
Sum	80.7251 keV ± 0.0022 keV

L_{III}	11.9193 keV ± 0.0005 keV
$K\alpha_1$	68.8061 keV ± 0.0018 keV
Sum	80.7254 keV ± 0.0023 keV

The close agreement of the sums compared with the limits of error is explained by the fact that the energy difference between the close α_1 and α_2 lines is more accurately determined than the absolute values of the energies.

3.3. *Discussion of errors*

The main errors in the edge determinations are introduced with the uncertainties in the I_l, I_k and I_b determinations. Fluctuations in the van de Graaff generator voltage and current caused variations in the primary intensity. These were to a large extent compensated by the monitor, and during the measurements the primary intensity was checked every second point and the intensity values corrected accordingly. Nevertheless the intensity measurements are considerably more uncertain than would be expected from count statistics. The scattering of the points around the straight lines in the diagram, Fig. 2, indicates maximal errors of 5 % in the background and 2 % in the limiting intensities as being representative. A general analysis of the influence of intensity and background errors on the wavelength position of the inflexion point is too complex, but calculations for a few experimental curves have shown the above errors to give a maximal error in the edge position of about one second of an arc. In comparison with this, the accidental errors in the readings from the spectrometer scale and the position determination of the U $K\alpha_1$ reference line are less important. The observed scattering of the points in the diagram of Fig. 3 is thus fully accounted for. From this diagram the extrapolated absorption limit value and the value of the shift are determined by a least squares fit. The corresponding errors are estimated from the diagram as $\pm 0.4''$ and $\pm 0.4''$ shift/0.1 mm. To the wavelength error is then added the appropriate uncertainties in the scale division and the Bragg angle used for U $K\alpha_1$. A total error in the Au K determination can then be given as $0.8''$, viz. 5 eV. The errors assigned to the Au $K\alpha_1$, α_2 values have been previously discussed [2].

3.4. *Conclusions*

As a comment on the above results it might be stated that when a high resolution spectrometer,[1] like the present one, is employed, and the optimal absorber thickness according to Sandström [11], here 0.10 mm, is used, the thickness effect is a noticeable contribution to the uncertainties encountered in direct K edge measurements of the above kind.

It is seen that the energy values of $(K\alpha_1 + L_{III})$ and $(K\alpha_2 + L_{II})$ agree within 0.5 eV. The mean of these two figures differs, however, by 5 eV from the value

---

[1] Preliminary measurements, earlier reported [3] with use of an arrangement of about half the resolution of the present spectrometer, yielded a value for the shift of 0.043 XU/0.1 mm for W K, or twice as much as the present value.

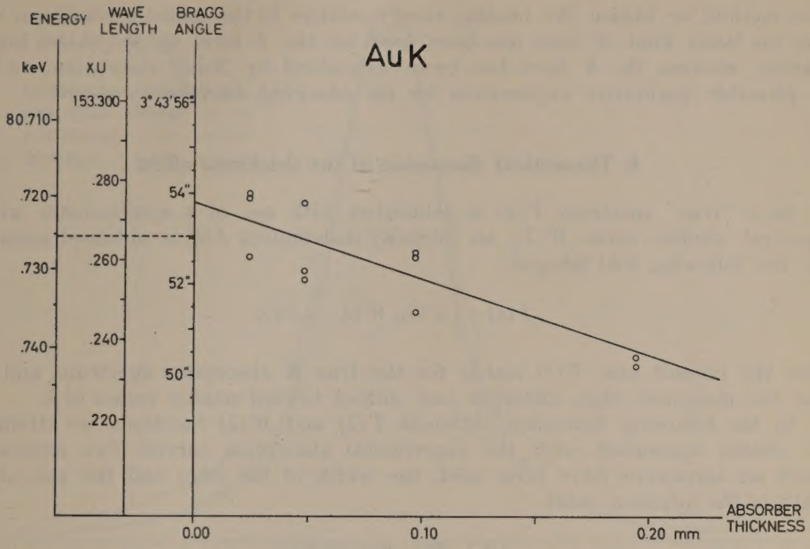

Fig. 3. Bragg angle, wavelength, and energy of inflexion points of the experimental curves given as functions of absorber thickness. The thickness effect is clearly demonstrated. The horizontal dashed line represents the mean of the $(K\alpha_1 + L_{III})$ and $(K\alpha_2 + L_{II})$ values.

of the *K* limit directly obtained. As the difference is within the limits of accuracy, it might be accidental. It should be pointed out, however, that the *K* level energy directly measured has the lower value. A similar discrepancy of a few electron volts has been found by Sokolowski [14] for *K* levels of fourth-period elements between her data and previous determinations from X-ray absorption edges. (For *L*-levels of heavier elements the X-ray determinations are too uncertain to permit a comparison.) The reason for this discrepancy can be sought in the different methods employed. Sokolowski measures the kinetic energy, E_k, of electrons obtained by photoelectric effect when a metal is irradiated by monochromatic X-rays of energy E_x. E_k is the energy of the electrons as they enter the magnetic analyser, referred to the grounded vacuum chamber of the spectrometer. To obtain the atomic binding energy as it is conventionally defined (the energy difference between the atomic level in question and the Fermi level of the metal), the work function is subtracted from the difference $(E_x - E_k)$.

For the case of X-ray measurements of atomic levels, by determinations of the absorption edge, as for example in the present work, a complication arises which has recently been stressed by Parratt [8]. As an electron is lifted out of an inner shell by photoelectric effect, the electric field of the atom, due to the nucleus and the screening electrons, is changed. This leads to a change in the outer atomic levels. The orbitals will be shifted closer to the nucleus, forming excitation orbitals of lower energy. The first unoccupied level of the atom will therefore have a lower energy than the Fermi level of the assembly of undisturbed atoms of the metal. The inflexion point of an absorption edge will consequently represent the binding energy of a disturbed atom, whereas by the photo electron method we obtain the binding energy relative to the undisturbed Fermi level. As the latter kind of data has been used for the L level values in this investigation, whereas the K level has been determined by X-ray absorption, we have a plausible qualitative explanation for the observed discrepancy above.

4. Theoretical discussion of the thickness effect

As a "true" spectrum $T(\lambda)$ is delineated with use of a spectrometer with a spectral window curve $W(\lambda)$, an intensity distribution $I(\lambda)$ is obtained according to the following fold integral:

$$I(\lambda)=\int_0^\infty T(\lambda_s)\,W(\lambda-\lambda_s)\,d\lambda_s. \tag{3}$$

For the present case $T(\lambda)$ stands for the true K absorption spectrum, and $I(\lambda)$ for the measured edge, distorted and shifted toward smaller values of λ.

In the following discussion, different $T(\lambda)$ and $W(\lambda)$ functions are attempted to obtain agreement with the experimntal absorption curves. Two criteria for such an agremeent have been used, the width of the edge and the size of the shift of the inflexion point.

4.1. *Window models*

The components which enter into the spectrometer window are a rectangular slit of known width, here 10″, and a crystal diffraction pattern of unknown shape and width. The diffraction pattern of a perfect unstressed crystal in the Laue case is the Lorentz curve: $1/(1+x^2)$. For an elastically curved crystal a much wider pattern, with a shape more similar to the Gaussian function, is obtained. The reason for this can be thought of in terms of the mosaic picture [16] where a large number of crystal domains, each of which giving the narrow Lorentz pattern, are oriented in a Gaussian distribution around the mean direction. An alternative explanation has been put forward by Berreman [4], suggesting extremely slight curvatures of the reflecting atomic planes as being the reason for the mosaic behavior.

Three diffraction pattern models were prepared:

(1) a pure Lorentzian,
(2) an intermediate fold of a Lorentzian and a Gaussian of the four-fold width, and
(3) a pure Gaussian curve.

For all the three model curves a width at half maximum of 10″ was assumed, and folds with the slit rectangle were calculated. The resulting curves showed the following widths:

(1) 14.2″, (2) 13.5″, (3) 12.5″.

For simplicity the curves were normalized to 13.5″ width, and were thus used as spectrometer window models. The spectrometer window in essentially the same for the two wavelength regions of Au K and Au $K\alpha_1$.

In order to check the assumptions leading to the above window models, three folds were now made with a true Au $K\alpha_1$ emission line, which was assumed

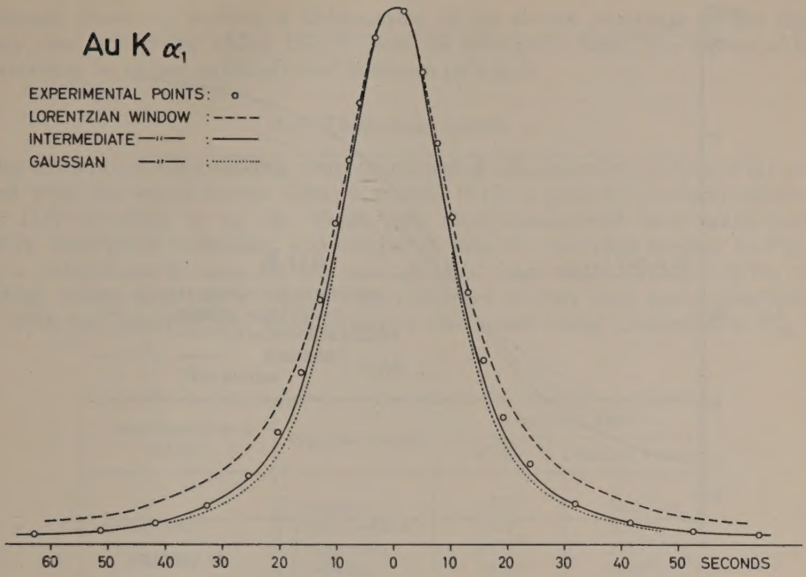

Fig. 4. The Au $K\alpha_1$ line according to three assumed spectrometer windows. Experimental points are plotted after height normalisation only.

to be of a Lorentzian shape and a width of 58 eV, according to Ramberg & Richtmyer [9]. The result is shown, after height normalization, in Fig. 4 together with experimental points for a spectrometer recording of this line. The agreement with respect to line width is regarded as a justification of the above assumptions.

4.2. *Absorption edge models*

The assumption of equidistant energy levels with equal transition probabilities in the valence band above the Fermi level leads to an arc tan variation for the absorption coefficient at the absorption limit according to Richtmyer, Barnes & Ramberg [10]. We know, however, that such an assumption is not valid. Variations in level density cause the Kossel–Kronig structure, apparent in L and M absorption spectra. For a K edge, this structure is not resolved, and can be expected to show only as a slight modification of the arc tan dependence. Therefore, as a first approximation, a pure arc tan variation was used as a basis for the absorption edge models. Two models were made, both representing 0.1 mm of gold absorber, adapted to the experimental μ_l and μ_k values, but with different widths, the one being equal to and the other half of the width of the window curves, viz. $13.5''$ and $6.8''$ respectively. The Au K width according to Ramberg & Richtmyer [9], 54 eV, makes $9.0''$, an intermediate value. A third edge model was also attempted in order to find out the effect on the shift if a variation in level density is taken into account. This model we obtained from the last of those

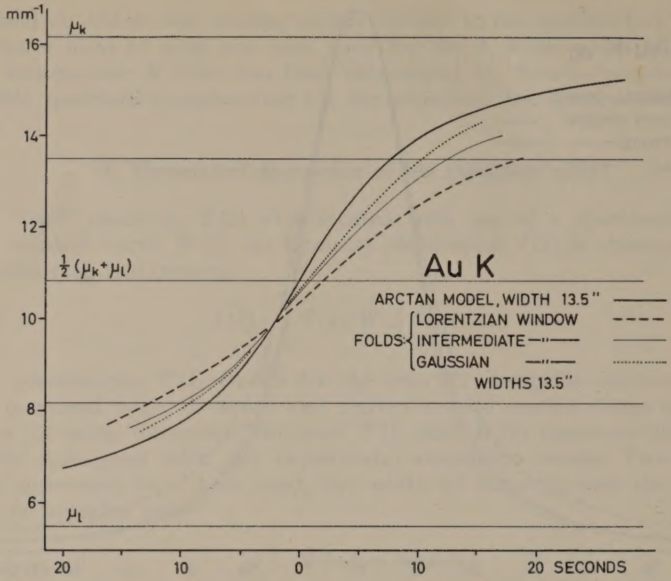

Fig. 5. Theoretical curves, showing a pure arc tan function and how this is distorted when recorded by three spectrometer windows. The broadening and shift of the edge are apparent.

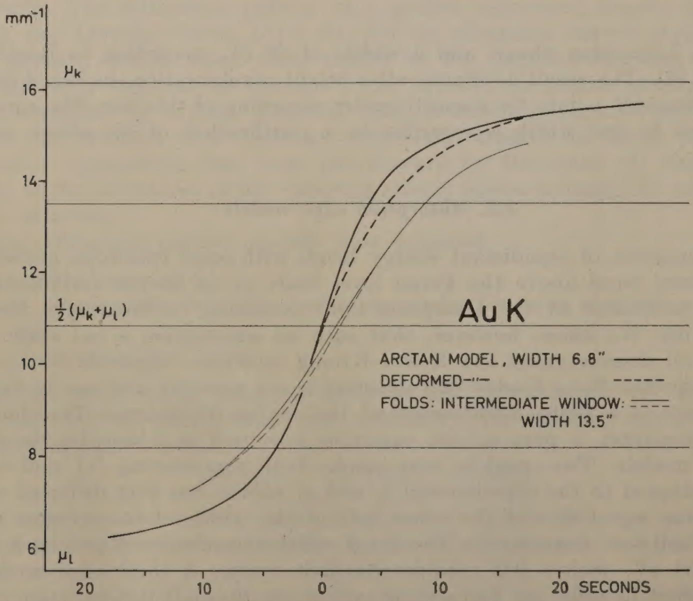

Fig. 6. Theoretical curves showing a pure arc tan and a deformed arc tan function, and how these are distorted when recorded by the intermediate spectrometer window.

mentioned above by making a deformation of the arc tan variation on the high-energy side, stretching about 150 eV from the absorption limit. The extent of the deformation is rather arbitrary and is shown in Fig. 6.

4.3. *Theoretical results*

The absorption edge models were transformed into intensity curves, $T(\lambda)$, and folded with the spectrometer window models $W(\lambda)$ to give the intensity distributions $I(\lambda)$ according to eq. (3). These were then transformed back to the variations in absorption coefficient, and compared with the true edge models. In Fig. 5 such a comparison is seen for the case of 13.5″ edge width. Table 3 gives the resulting widths and size of shifts. The deformed arc tan edge model was folded only with the intermediate window model, the result being illustrated in Fig. 6.

Table 3.

Edge model and width	Window model	Resulting edge	
		Width	Shift/0.1 mm
arc tan 13.5″	Gaussian	17.1″	0.61″
	Intermediate	19.4″	0.85″
	Lorentzian	27.2″	1.69″
arc tan 6.8″	Gaussian	11.9″	0.83″
	Intermediate	13.3″	1.07″
	Lorentzian	19.1″	1.69″
deformed (6.8″)	Intermediate	12.6″	1.36″
Experimental values		12.8″ ± 2.6″	1.77″ ± 0.40″

The size of the shift is to a large extent determined by the remote "tails" of the spectrometer window, which is seen if the figures in table 3 for a Gaussian and a Lorentzian window are compared. From the experimental value of the shift one concludes that the "tails" of the unknown spectrometer window are probably higher than for the intermediate window model. A pure Lorentzian window, however, gives too high values for edge width. It is also seen from Fig. 4 that, as regards the tails, a Lorentzian window is not compatible with observation. If we compare the results for the two arc tan edge models, we find the best agreement with experiment for 41 eV K level width. The value of 54 eV given by Ramberg & Richtmyer [9] is an extrapolation of an experimental determination of the K level width for W (74), assuming a Z^4 dependence, and may be in error. The arbitrary deformation of the 41 eV edge, shown in Fig. 6, is seen to add 27 % to the shift obtained with the pure arc tan edge. As it appears from the last line of Table 3 the best agreement is obtained assuming a deformed edge model and the intermediate window model.

Precise information on the shape of the true edge might be obtained from L and M absorption spectra and knowledge of the K level width. Together with experimental data regarding the observed shape of the edge, this would, in principle, be sufficient for a calculation of the spectrometer window curve according to eq. (3). Parratt *et al.* [7] have succeeded in this, using an ionic compound of lighter elements, KCl. In the present case, however, the wide K level has smoothed out all structural details which might serve as criteria for the influence of the spectrometer window on the true spectrum. In addition, the spectrometer resolution is too low compared with the width of the absorption edge to permit the necessary experimental accuracy.

SUMMARY

An X-ray determination of the K absorption edge of Au with a spectral resolution of 0.1 % and with use of different absorber thicknesses is reported. A shift of the edge towards shorter wavelengths for increased absorber thickness of 0.020 XU per 0.1 mm absorber is found. Extrapolation to zero thickness gives Au K: 153.275 ± 0.010 XU, or 80.7205 ± 0.005 keV. The Au $K\alpha$ emission lines are measured and the corresponding L level energies obtained by other investigators are added:

$$\mathrm{Au}K\alpha_1 + L_{\mathrm{III}}: \ 80.7254 \pm 0.0023 \text{ keV},$$
$$\mathrm{Au}K\alpha_2 + L_{\mathrm{II}}: \ 80.7251 \pm 0.0022 \text{ keV}.$$

The size of the shift is theoretically accounted for with certain assumptions on the spectrometer window.

ACKNOWLEDGEMENTS

The authors are much indebted to Prof. Per Ohlin and Prof. Kai Siegbahn for their interest and support. We also wish to thank Fil. lic. Bertil Nordfors, Fil. lic. Carl Nordling and Fil. lic. Evelyn Sokolowski for stimulating discussions. Support from the Swedish Natural Science Research Council is gratefully acknowledged.

Institute of Physics, Uppsala, Sweden.

REFERENCES

1. Beckman, O., Arkiv för Fysik *9*, 495 (1955).
2. Beckman, O., Bergvall, P., and Axelsson, B., Arkiv för Fysik *14*, 419 (1958).
3. Bergvall, P., Beckman, O., and Axelsson, B., Arkiv för Fysik *13*, 257 (1958).
4. Berreman, D. W., Phys. Rev. *110*, 992 (1958).
5. Ingelstam, E., Nova Acta Reg. Soc. Sci. Uppsala *5* (1937).
6. Jay, A. H., Proc. Roy. Soc. *142*, 237 (1933).
7. Parratt, L. G., Hempstead, C. F., and Jossem, E. L., Phys. Rev. *105*, 1228 (1957).
8. Paratt, L. G., "Electronic band structure of solids by the method of experimental x-ray spectroscopy", ASTIA Technical Report No. 8 (1958).
9. Ramberg, E. G., and Richtmyer, F. K., Phys. Rev. *51*, 913 (1937).
10. Richtmyer, F. K., Barnes, S. W., and Ramberg, E., Phys. Rev., *46*, 843 (1934).
11. Sandström, A. E., Z. Physik *65*, 632 (1930).
12. Sandström, A. E., Handbuch der Physik, S. Flügge, vol. XXX, p. 78.
13. Sokolowski, E., Nordling, C., and Siegbahn, K., Phys. Rev. *105*, 1676 (1957); Arkiv för Fysik *12*, 301 (1957).
14. Sokolowski, E., Arkiv för Fysik *15*, 1 (1959).
15. Victoreen, J. A., J. Appl. Phys. *20*, 1141 (1949).
16. Zachariasen, W. H., Theory of X-ray Diffraction in Crystals. New York, 1945.

Tryckt den 12 maj 1959

Uppsala 1959. Almqvist & Wiksells Boktryckeri AB